

PATENT SPECIFICATION

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 (72) Inventors GORDON FRANK BRADLEY and DAVID PRICE



(54) AZO PIGMENT COMPOSITIONS

SPECIFICATION NO 1359459

INVENTORS: GORDON FRANK BRADLEY & DAVID PRICE

By a direction given under Section 17 (1) of the Patents Act 1949 this application proceeded in the name of Ciba-Geigy AG., A Swissbody Corporate, of Basle, Switzerland.

THE PATENT OFFICE

R 76331/4

to be performed, to be particularly defined in and by the following statement:—

The suitability of a pigment for dispersion in any given medium for any particular use may be assessed in terms of the rheological properties, tinctorial strength, gloss, transparency, hue and wettability/dispersibility characteristics exhibited by the pigment in the medium. In general terms all these can be related to the crystallographic properties of the pigment and to the surface properties of the pigment particles, which are to a considerable extent interdependent.

It is known that the surface of organic pigment particles can be modified by absorbing onto the particles a wide variety of surface active agents or solvents, or by having such materials present during the formation of the pigment. By changing the surface of the particles in this manner it has been found possible to change the rheological properties of the pigment, and hence the degree of dispersion obtainable in printing ink and paint media, with corresponding changes in the transparency and gloss of the pigment.

We have now discovered a further method by means of which organic pigments with improved properties can be obtained. According to the present invention there is provided a pigment composition comprising particles of a first azo pigment wholly or partially coated with a second azo pigment, the two pigments being derived from different coupling components and one of the pigments being derived from a tetrazotised benzidine compound and the other pigment being derived from the same benzidine compound or is a different disazo pigment or is a monoazo pig-

ment. benzidines can be used; for example, pigments have been prepared from tetrachlorobenzidines. Examples of coupling agents which have been used are acetoacetanilide, acetoacet - o - toluidine, acetoacet - p - toluidide, acetoacet - o - anisidide and acetoacet - 2,4 - xylidide.

The other organic pigment may be formed, for example, by coupling a diazotised nitroaniline with an acetoacetarylamine.

Azo pigments are normally produced by coupling the diazotised component with the coupling agent in acid aqueous medium. After the coupling, the reaction mixture is boiled, and the pigment worked up.

Two parameters of the resulting pigment are of importance, the mean primary particle size and the mean crystallite size within each particle, and it is found that better rheological properties are obtained when the pigments are incorporated in printing ink media for any given mean primary particle size of the pigment if the mean crystallite size is large, and indeed approaches the mean primary particle size. In the present invention we take the basic core pigment and modify its surface with a complete or parallel coating of another pigment of similar structure. Thus, for example, the pigment prepared by coupling acetoacet - o - anisidide with 3:3' - dichlorobenzidine is in the form of small crystallites (amorphous to X-ray powder photograph) and has poor flow properties in printing inks, whereas the pigment prepared by coupling acetoacet - m - xylidide with 3:3' - dichlorobenzidine is in the form of large crystallites and has good flow properties; a pigment composition of

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(54) AZO PIGMENT COMPOSITIONS

(71) We, CIBA-GEIGY (UK) LIMITED, a British Company, whose Registered Office address is 30 Buckingham Gate, London SW1 6EH (formerly 42 Berkely Square, London, W.1.) (formerly known as Geigy (U.K.) Limited, a British Company, whose Registered Office address was Simonsway, Manchester 22), do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The suitability of a pigment for dispersion in any given medium for any particular use may be assessed in terms of the rheological properties, tinctorial strength, gloss, transparency, hue and wettability/dispersibility characteristics exhibited by the pigment in the medium. In general terms all these can be related to the crystallographic properties of the pigment and to the surface properties of the pigment particles, which are to a considerable extent interdependent.

It is known that the surface of organic pigment particles can be modified by absorbing onto the particles a wide variety of surface active agents or solvents, or by having such materials present during the formation of the pigment. By changing the surface of the particles in this manner it has been found possible to change the rheological properties of the pigment, and hence the degree of dispersion obtainable in printing ink and paint media, with corresponding changes in the transparency and gloss of the pigment.

We have now discovered a further method by means of which organic pigments with improved properties can be obtained. According to the present invention there is provided a pigment composition comprising particles of a first azo pigment wholly or partially coated with a second azo pigment, the two pigments being derived from different coupling components and one of the pigments being derived from a tetrazotised benzidine compound and the other pigment being derived from the same benzidine compound or is a different disazo pigment or is a monoazo pigment,

the second azo pigment having been formed in the presence of particles of the first azo pigment.

The azo pigment derived from a tetrazotised benzidine compound may be formed, for example, by coupling tetrazotised 3:3' - dichlorobenzidine itself or a tetrazotised 3:3' - dichlorobenzidine bearing further substituents in the aromatic nuclei with an acetoacetyl- amide. Normally 3:3' - dichlorobenzidine itself is used, but substituted 3:3' - dichlorobenzidines can be used; for example, pigments have been prepared from tetrachlorobenzidines. Examples of coupling agents which have been used are acetoacetanilide, acetoacet - o - toluidine, acetoacet - p - toluidide, acetoacet - o - anisidide and acetoacet - 2,4 - xylidide.

The other organic pigment may be formed, for example, by coupling a diazotised nitroaniline with an acetoacetyl- amide.

Azo pigments are normally produced by coupling the diazotised component with the coupling agent in acid aqueous medium. After the coupling, the reaction mixture is boiled, and the pigment worked up.

Two parameters of the resulting pigment are of importance, the mean primary particle size and the mean crystallite size within each particle, and it is found that better rheological properties are obtained when the pigments are incorporated in printing ink media for any given mean primary particle size of the pigment if the mean crystallite size is large, and indeed approaches the mean primary particle size. In the present invention we take the basic core pigment and modify its surface with a complete or parallel coating of another pigment of similar structure. Thus, for example, the pigment prepared by coupling acetoacet - o - anisidide with 3:3' - dichlorobenzidine is in the form of small crystallites (amorphous to X-ray powder photograph) and has poor flow properties in printing inks, whereas the pigment prepared by coupling acetoacet - m - xylidide with 3:3' - dichlorobenzidine is in the form of large crystallites and has good flow properties; a pigment composition of

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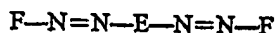
particles of acetoacet - *o* - anisidide coupled to 3:3' - dichlorobenzidine particles coated with acetoacet - *m* - xylidide coupled to 3:3' - dichlorobenzidine combines the desirable properties of each pigment.

Pigment compositions according to the invention may be prepared in the following manner. A slurry of the first pigment is prepared, and then the second pigment is precipitated in the slurry, so that some of the second pigment species will preferentially precipitate on to the nuclei already present, that is the particles of the first pigment, and form a coating on them. It is believed that some of the second organic pigment on formation during a precipitation process grows onto existing crystallites of the first pigment at high energy active sites such as dislocation sites. This coating action occurs even if the second pigment is only present in small proportions. This process is particularly successful in the case of azo pigments; the first pigment can be prepared in a coupling solution, and then the second pigment prepared in the same solution without the necessity for isolation of the first pigment. Different coupling agents are used for the two pigments.

Evidence that coating of the pigment core is achieved may be obtained as follows. If a pigment core of acetoacet - *m* - xylidide coupled to tetrazotised 3:3' - dichlorobenzidine is treated in such a way that one might assume, according to our invention, that a pigment coating of acetoacet - *o* - anisidide coupled to tetrazotised 3:3' - dichlorobenzidine would be formed on it, and if the system is boiled at the slurry stage the crystallite growth of the core is inhibited by the pigment coating. This is shown by X-ray powder photography. On the other hand, if a physical mixture of slurries obtained by mixing freshly prepared acetoacet - *m* - xylidide coupled to tetrazotised 3:3' - dichlorobenzidine and freshly prepared acetoacet - *o* - anisidide coupled to tetrazotised 3:3' - dichlorobenzidine, that is not obtained by co-precipitation, is boiled, no inhibition of growth of the crystallite particles in the core can be observed.

The effect of the invention is to form a coating or partial coating of a second azo pigment onto a core of a first pigment. The optical properties of the pigment core are not dramatically altered, since the optical properties of the composition will be somewhere between the properties of each pigment. What is in effect achieved is a composition with the optical properties of a first pigment but the surface properties of a second pigment when the coating pigment is present in small quantities.

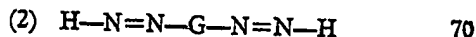
In the case of diazo pigments such as the benzidine yellows the core pigment can be represented as



where E is the tetrazo component and F is the coupling component. This can be coated with



where H is a coupling component different from that used in the core pigment, or



where G is a tetrazo component different from that used in the core pigment and the coupling component differs from that used in the core pigment.

It is also possible to have a monoazo pigment core coated by a benzidine disazo pigment derived from a different coupling component, or vice versa.

A further point which has been noted is that the core pigment may induce the coating pigment to adopt a particular crystal modification different from that normally formed by the coating pigment. In this case the pigment forming the core may form only a minor proportion of the final composite pigment. The action, in this case, of the core forming pigment is that of a "seed" which controls the way the remaining coating pigment is precipitated from solution. The properties of the resulting pigment composition may therefore be controlled.

Pigment compositions according to the invention may be treated at any stage with any of the conventional solvents or surface active agents used to modify surface properties of pigments. Thus the core pigment may be formed in the presence of conventional additives, or treated with them after formation; the coating pigment may be formed in the presence of conventional additives or the pigment composition may be treated with conventional additives. Conventional treatments will include surface active agent, solvent and resination treatments and treatments with amines and with dyestuffs as described in our copending applications, Nos. 21754/70, 34427/70, 34428/70 and 34429/70; (Serial Nos. 1356253), (1356254) and (1356253).

Some Examples will now be given, all parts and proportions being by weight unless otherwise stated.

Example 1

A tetrazonium solution was made from 19.0 parts of 3:3' - dichloro - benzidine in 450 parts of water.

16.5 parts of acetoacetorthoanisidide were dissolved in 225 parts of water containing 3.2 parts of sodium hydroxide. Dilute acetic acid was run into the solution until the pH was below 7.

The tetrazonium solution was slowly added to the anisidide solution so that there was no substantial excess of tetrazo at any time, the pH being controlled at 4.0-4.5 by adding

10% sodium hydroxide solution, until all the coupling component had reacted.

16.5 parts of acetoacetmetaxylidide were dissolved in 225 parts of water containing 3.2 parts of sodium hydroxide, and this solution added to the coupling reaction, keeping the pH below 7.0.

The remainder of the tetrazonium solution was then run in slowly as before avoiding any excess of tetrazonium salt and maintaining pH greater than 4.0 by addition of 10% caustic soda solution.

The resulting slurry was boiled for 1 hour and the pigment composition was then isolated by filtering, washing the filter-cake free of water-soluble impurities and drying at 50°C.

The pigment composition was found to have mean crystallite size of 0.06 μ by X-ray powder diffraction and to have excellent flow, transparency, gloss and dispersibility properties in printing ink media, better than those of a simple physical mixture of the two pigments.

If pigment slurries of acetoacet-ortho-anisidide coupled to 3:3' - dichlorobenzidine and of acetoacet - meta - xylidide coupled to 3:3' - dichlorobenzidine are prepared in separate vessels and then mixed, and boiled and worked up, the mean crystallite size of the particles is below 0.03 μ , amorphous to X-rays. The pigment composition prepared in this way by mixing slurries has poor rheological properties when introduced into letter press ink media.

Example 2

The procedure described in Example 1 was repeated except that the ratio of the coupling agents was altered from equal parts by weight to 4:1 molar acetoacet - *o* - anisidide to acetoacet - *m* - xylidide. After formation, the slurry of pigment composition was boiled with 5% by weight of dibenzyl ether.

The final pigment composition was isolated by filtering the slurry, washing the filter-cake free of water-soluble impurities and drying at 50°C.

When the final pigment composition was incorporated in a letterpress ink medium, its rheological properties were found to be superior to those of a conventional pigment formed by coupling acetoacet - *o* - anisidide and 3:3' - dichlorobenzidine with the same solvent treatment. As in Example 1, the pigment composition has superior properties to those of a pigment formed by mixing prepared slurries.

Example 3

The procedure described in Example 2 was repeated, except that the ratio of the coupling agents was altered to 1:4-molar acetoacet - *o* - anisidide to acetoacet - *m* - xylidide.

The pigment composition formed had better gloss and transparency when incorporated into letterpress ink medium than did the con-

ventional pigment formed by coupling acetoacet - *m* - xylidide and 3:3' - dichlorobenzidine with the same solvent treatment.

A physical mixture of the two pigments, prepared in separate vessels, mixed and worked up did not give the same advantageous gloss and transparency when incorporated in letterpress ink media.

Example 4

The procedure described in Example 2 was repeated except that acetoacetanilide was used instead of acetoacet - *m* - xylidide, and the ratio of the coupling agents was kept at 4:1 molar acetoacet - *o* - anisidide to acetoacetanilide.

The pigment composition formed had better rheological properties when incorporated into a letterpress ink medium than did the conventional pigment formed by coupling acetoacet - *o* - anisidide and 3:3' - dichlorobenzidine with the same solvent treatment. As in Example 1, the pigment composition has superior properties to those of a pigment formed by mixing prepared slurries.

Example 5

The procedure described in Example 2 was repeated except that the acetoacet - *m* - xylidide was replaced by an equal molar proportion of acetoacet - *o* - toluidide.

The pigment composition formed had better rheological properties when incorporated into a letterpress ink medium than did the conventional pigment formed by coupling acetoacet - *o* - anisidide and 3:3' - dichlorobenzidine with the same solvent treatment. As in Example 1, the pigment composition has superior properties to those of a pigment formed by mixing prepared slurries.

Example 6

The procedure described in Example 2 was repeated except that acetoacetanilide was used instead of acetoacet - *m* - xylidide, and the ratio of the coupling agents was altered to 1:3 molar acetoacet - *o* - anisidide to acetoacetanilide.

The pigment composition formed had better gloss and transparency when incorporated into letterpress ink medium than did the conventional pigment formed by coupling acetoacet-*o*-anisidide and 3:3' - dichlorobenzidine with the same solvent treatment.

Example 7

Coupling A

A tetrazonium solution was made from 27.4 parts of 3:3' - dichlorobenzidine in 600 parts of water.

19.4 parts of acetoacetanilide were dissolved in a coupling vessel containing 300 parts of water and 4.4 parts of sodium hydroxide. Dilute acetic acid was run into this solution until the pH was below 7.0.

The tetrazonium solution was slowly added to the acetoanilide suspension so that there was no substantial excess of tetrazonium salt at any time, the pH being controlled at 4.0—4.5 by adding a 10% sodium hydroxide solution, until the coupling component had reacted completely.

22.7 parts of acetoacet - *o* - anisidine were dissolved in 300 parts of water containing 4.4 parts of sodium hydroxide. This solution was run into the slurry in the coupling vessel simultaneously with the remainder of the tetrazonium solution, the pH being controlled at 4.0—4.5 during the coupling by the addition of the necessary amount of a 10% sodium hydroxide solution. No substantial excess of tetrazonium salt was allowed at any time during this second coupling.

The resultant pigment slurry was then boiled for 1 hour and the pigment was then isolated by filtering, washing the filter-cake free of water-soluble impurities and drying at 50°C.

Coupling B

A tetrazonium solution was made from 27.4 parts of 3:3 - dichlorobenzidine in 600 parts of water. Separate pigment slurries were prepared from this as follows:—

Slurry 1

19.4 parts of acetoacetanilide were dissolved in 300 parts of water containing 4.4 parts of sodium hydroxide. Dilute acetic acid was run into the solution until the pH was below 7.

300 parts of the tetrazonium solution were slowly added to the acetoacet-anilide suspension so that there was no substantial excess of tetrazo at any time, the pH being controlled at 4.0—4.5 by adding 10% sodium hydroxide solution, until all the coupling component had reacted.

Slurry 2

22.7 parts of acetoacet - *o* - anisidine were dissolved in 300 parts of water containing 4.4 parts of sodium hydroxide. Into the coupling vessel was added 5.0 parts sodium acetate and 250 parts of water.

The remaining 300 parts of the tetrazo solution were slowly added with the anisidine suspension to the coupling vessel so that there was no substantial excess of tetrazo at any time, the pH being controlled at 4.0—4.5 by adding 10% sodium hydroxide solution, until all the coupling component had reacted.

Slurries 1 and 2 were mixed together and the resultant pigment slurry was then boiled for 1 hour and the pigment was then isolated by filtering, washing the filter-cake free of water-soluble impurities and drying at 50°C.

When incorporated into a letterpress ink varnish medium, the pigment composition resulting from Coupling A, the process according to the invention, is more transparent than

the pigment resulting from Coupling B, a process yielding merely a physical mixture of pigments.

Example 8

Coupling A

A tetrazonium solution was prepared from 25.3 parts of 3:3' - dichlorobenzidine in 500 parts of water.

17.4 parts of 1 - phenyl - 3 - methyl - 5 - pyrazolone were dissolved in 250 parts of water containing 4.1 parts of sodium hydroxide. Dilute acetic acid was run into the solution until the pH was below 7.

The tetrazonium solution was slowly added to the pyrazolone slurry in a coupling vessel so that there was no substantial excess of tetrazonium at any time, the pH being controlled at 4.0—4.5 by adding 10% sodium hydroxide solution until all the coupling component had reacted.

20.7 parts of acetoacet - *o* - anisidine were dissolved in 250 parts of water containing 4.1 parts of sodium hydroxide, and this solution added to the coupling vessel simultaneously with dilute acetic acid keeping the pH below 7.0.

The remainder of the tetrazo solution was then run in slowly as before avoiding any excess of tetrazo and maintaining pH greater than 4.0 by addition of 10% caustic soda solution.

The resultant pigment slurry was boiled for 1 hour and the pigment was then isolated by filtering, washing the filter-cake free of water-soluble impurities and drying at 50°C.

Coupling B

A tetrazo solution was prepared from 25.3 parts of 3:3 - dichlorobenzidine in 500 parts of water. Separate pigment slurries were prepared from this as follows:

Slurry 1

17.4 parts of 1 - phenyl - 3 - methyl - 5 - pyrazolone were dissolved in 250 parts of water containing 4.1 parts of sodium hydroxide. Dilute acetic acid was run into the solution until the pH was below 7.

250 parts of the tetrazonium solution were slowly added to the pyrazolone suspension so that there was no substantial excess of tetrazonium at any time, the pH being controlled at 4.0—4.5 by adding 10% sodium hydroxide solution, until all the coupling component had reacted.

Slurry 2

20.7 parts of acetoacet - *o* - anisidine were dissolved in 250 parts of water containing 4.1 parts of sodium hydroxide. Dilute acetic acid was run into the solution until the pH was below 7.

The remaining 250 parts of the tetrazonium solution were slowly added to the anisidine suspension so that there was no substantial

excess of tetrazonium at any time, the pH being controlled at 4.0—4.5 by adding 10% sodium hydroxide solution, until all the coupling component had reacted.

5 Slurries 1 and 2

were mixed together and the resultant slurry was then boiled for 1 hour and the pigment was then isolated by filtering, washing the filter-cake free of water-soluble impurities and drying at 50°C.

Coupling C

A tetrazo solution was prepared from 25.3 parts of 3:3' - dichlorobenzidine in 500 parts of water.

15 17.4 parts of 1 - phenyl - 3 - methyl - 5 - pyrazolone and 20.7 parts of acetoacet - o - aniside were dissolved in 500 parts of water containing 8.2 parts of sodium hydroxide. Dilute acetic acid was run into the solution until the pH was below 7.

20 The tetrazonium solution was slowly added to the above mixed suspension so that there was no substantial excess of tetrazonium at any time, the pH being controlled at 4.0—4.5 by adding 10% sodium hydroxide solution, until all the coupling component had reacted.

30 The resultant pigment slurry was boiled for 1 hour and the pigment was then isolated by filtering, washing the filter-cake free of water-soluble impurities and drying at 50°C.

35 When incorporated into a letterpress ink varnish medium, pigment composition from Coupling A gave superior transparency to the Coupling B product. The pigment composition from Coupling C would not be compared colouristically with the rest as its hue was much too yellow.

Example 9

40 i) A tetrazonium solution was made from 21.2 parts of o - toluidine (3:3' - dimethylbenzidine) in 500 parts of water.

45 ii) A tetrazonium solution was made from 25.3 parts of 3:3' - dichlorobenzidine in 500 parts of water.

iii) A solution was prepared of 37.6 parts of 1 - p - tolyl - 3 - methyl - 5 - pyrazolone in 500 parts of water and 11.6 parts of sodium hydroxide.

50 iv) A solution was prepared of 41.4 parts of acetoacet - o - aniside in 500 parts of water and 11.6 parts of sodium hydroxide.

Coupling A

55 Dilute acetic acid was run into solution iii until the pH fell below 7.0. Tetrazonium solution i) was added slowly so that there was no substantial excess of tetrazonium at any time, the pH kept at 4.0—4.5 by adding 10% sodium hydroxide solution, until all of the coupling component had reacted.

Solution iv) was run into the above coupled slurry and the pH kept below 7.0 by suitable addition of 10% sodium hydroxide solution. Finally tetrazonium solution ii) was slowly added and the pH controlled between 4.0 and 4.5 as above until all the coupling component had reacted.

The slurry was boiled for 1 hour and the pigment was then isolated by filtering, washing the filter-cake free of water-soluble impurities and drying at 50°C.

This is an example of the process according to the invention.

Coupling B

Solutions i) to iv) were prepared as above.

Dilute acetic acid was run into solution iii) until the pH fell below 7.0. Tetrazonium solution i) was added slowly, the pH being maintained at 4.0—4.5 as above.

Dilute acetic acid was run into solution iv) until the pH fell below 7.0. Tetrazonium solution ii) was slowly added, the pH being maintained at 4.0—4.5 as above.

The two coupled slurries were then mixed, the combined slurry was boiled for 1 hour, and the pigment was then isolated by filtering, washing the filter-cake free of water-soluble impurities and drying at 50°C.

This pigment is classed as a physical mixture.

Coupling C

Solutions i) to iv) were prepared as above.

Dilute acetic acid was run into a mixture of solutions iii) and iv) until the pH was below 7.0. Tetrazonium solutions i) and ii) were mixed and the combined solution was added slowly, the pH being maintained at 4.0—4.5 as above.

The slurry was then boiled for 1 hour and the pigment was then isolated by filtering, washing the filter-cake free of water-soluble impurities and drying at 50°C.

This process is an example of a mixed coupling.

When incorporated into a letterpress ink varnish medium the pigment composition from Coupling A had tinctorial strength, transparency and gloss advantages over that from Coupling B, and was similar in hue.

The pigment composition produced from Coupling C when incorporated into the same letterpress ink varnish medium gave a much yellower hue and could not be compared colouristically with either of the products of Couplings A or B. This may be due to the presence of asymmetrical bisarylide compounds in the final pigment composition which will alter the hue of the pigment composition.

Example 10

i) A tetrazonium solution was prepared from 50.6 parts of 3:3' - dichlorobenzidine in 1000 parts of water.

- ii) A solution was prepared of 37.6 parts of 1 - *p* - tolyl - 3 - methyl - 5 - pyrazolone in 500 parts water and 11.6 parts sodium hydroxide.
- 5 iii) A solution was prepared of 35.8 parts of 1 - phenyl - 3 - methyl - 5 - pyrazolone in 500 parts water and 11.6 parts sodium hydroxide.

Coupling A

- 10 Dilute acetic acid was added to solution iii) until the pH was below 7.0. The tetrazonium solution i) was slowly added to this slurry as described in Example 8 maintaining the pH between 4.5 and 5.0 until all the coupling component had reacted.

- 15 Solution ii) was slowly added simultaneously with 10% acetic acid solution to keep pH below 7.0. The remainder of solution i) was slowly added at maintained pH of 4.5—5.0.

- 20 The final slurry was boiled for 1 hour; the pigment isolated by filtering, washing free of water-soluble impurities and drying at 50°C.

- 25 This is an example of the process according to the invention.

Coupling B

Solutions i) to iii) were prepared as above. Separate pigment slurries were prepared as follows:—

- 30 Dilute acetic acid was added to solution iii) until the pH was below 7.0. Half of tetrazonium solution i) was run in whilst maintaining the pH between 4.5—5.0 by suitable addition of 10% sodium hydroxide solution.

- 35 Dilute acetic acid was added to solution ii) until the pH was below 7.0. The remainder of the tetrazonium solution i) was slowly added whilst maintaining the pH between 4.5—5.0.

- 40 The two slurries were mixed and the combined slurry boiled for 1 hour; the pigment was isolated by filtering, washing free of water-soluble impurities and drying at 50°C.

- 45 The pigment is classed as a physical mixture.

When incorporated into a letterpress varnish medium the pigment composition of Coupling A gave an ink of enhanced tinctorial strength to that from Coupling B.

- 50 X-ray Powder Diffraction studies on both

samples indicated that the pigment composition from Coupling A was of smaller crystallite size than that of Coupling B.

WHAT WE CLAIM IS:—

1. A pigment composition comprising particles of a first azo pigment wholly or partially coated with a second azo pigment, the two pigments being derived from different coupling components and one of the pigments being derived from a tetrazotised benzidine compound and the other pigment being derived from the same benzidine compound or is a different disazo pigment or is a mono-azo pigment, the second azo pigment having been formed in the presence of particles of the first azo pigment.

2. A pigment composition according to claim 1 substantially as hereinbefore described with particular reference to any of Examples 1 to 5.

3. A pigment composition according to claim 1 substantially as hereinbefore described with particular reference to any of Examples 6 to 10.

4. A process for the preparation of a pigment composition according to claim 1 in which a slurry of a first azo organic pigment is prepared, and then a second azo pigment is precipitated in the slurry.

5. A process according to claim 4 or 5 in which the first organic pigment is subjected to treatment with surface-active agent, solvent or resin before being coated.

6. A process according to claim 4 substantially as described in any one of Examples 1 to 5 herein.

7. A process according to claim 4 substantially as described in any one of Examples 6 to 10 herein.

8. A pigment composition according to claim 1 prepared by the process claimed in any one of claims 4 to 6.

9. A pigment composition according to claim 1 prepared by the process claimed in claim 7.

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